



University of Tennessee, Knoxville

TRACE: Tennessee Research and Creative Exchange

Chancellor's Honors Program Projects

Supervised Undergraduate Student Research
and Creative Work

Spring 5-2005

Rheology of Polyhydroxyalkanoates: A Study of a Class of "Green" Polymers

Kari Elizabeth Tjader
University of Tennessee - Knoxville

Follow this and additional works at: https://trace.tennessee.edu/utk_chanhonoproj

Recommended Citation

Tjader, Kari Elizabeth, "Rheology of Polyhydroxyalkanoates: A Study of a Class of "Green" Polymers" (2005). *Chancellor's Honors Program Projects*.
https://trace.tennessee.edu/utk_chanhonoproj/922

This is brought to you for free and open access by the Supervised Undergraduate Student Research and Creative Work at TRACE: Tennessee Research and Creative Exchange. It has been accepted for inclusion in Chancellor's Honors Program Projects by an authorized administrator of TRACE: Tennessee Research and Creative Exchange. For more information, please contact trace@utk.edu.

Rheology of Polyhydroxyalkanoates: A Study of a Class of “Green” Polymers

Senior Honors Project
Kari Elizabeth Tjader
Chemical Engineering
Spring 2005

Faculty Mentor: Dr. Simioan Petrovan
Department of Chemical Engineering

This research was accomplished in conjunction with chemical engineering 410, a senior special-topics laboratory class, with partner Mary Airhart.

Table of Contents

List of Figures.....	iii
Summary.....	1
Introduction.....	2
Background.....	3
Experimental Method.....	7
Results and Discussion.....	8
Conclusions	16
References.....	17

List of Figures

Figure 1 -	Typical PHA Monomers.....	4
Figure 2 -	Diagram of Rheometer.....	4
Figure 3 -	Dynamic Strain Sweep for PHA A.....	9
Figure 4 -	Complex Viscosity of PHA A.....	10
Figure 5 -	Dynamic Moduli of PHA A.....	11
Figure 6 -	Master Curve for PHA A.....	12
Figure 7 -	Complex Viscosity of PHA B.....	13
Figure 8 -	Dynamic Moduli of PHA B.....	14
Figure 9 -	Comparison of Different Polymers.....	15

Summary

This study was completed for Chemical Engineering Senior Special Topics Laboratory, ChE 410. Its objective was to learn about rheology and how to do a rheological study by analyzing polyhydroxyalkanoates (PHAs), an emerging class of polymers. Two of the benefits of PHAs are that they are biodegradable and made from renewable resources. The study analyzed the viscosity of three samples of PHAs as a function of temperature and deformation rate. The information from this study was useful for the recommendation of using PHAs as replacements for some polymers that are processed by melt blowing.

Introduction

Polyhydroxyalkanoates (PHAs) are an important class of polymers that can be used as a biodegradable substitute for many synthetic plastics. They are desirable because of their sustainability and environmental friendliness. PHAs are synthesized by bacterial fermentation. Because oil is currently used in the production of synthetic polymers, the widespread use of PHAs could eventually decrease dependence on foreign oil.

As interest in the use of PHAs increases, industrial-scale processes are being developed to reduce their production cost. Related to the research on industrial-scale production, this study analyzes the rheometric properties of three separate samples of PHAs. Conclusions from this study contribute to the developing knowledge of the flow characteristics of PHAs as well as help in moving forward in the effort to replace synthetic plastics with a more attractive alternative.

Background

Rheology is the science of deformation and flow of material. It plays an important role in diverse fields such as polymer science, earth science, and food science. The world is made up of flowing materials. Some flow at high velocities—rivers and streams in processing plants. Some flow at low velocities—glaciers and the earth's plates.

The flow of some materials can be described with simple equations derived by Newton. For Newtonian materials flow is directly proportional to the force imposed on them or:

$$\frac{F}{A} = \mu \frac{V}{Y}$$

where F is force, A is area, V is velocity, Y is thickness of the fluid layer, and μ is viscosity. In this simple correlation, viscosity does not change as the surroundings change (temperature, pressure) or as the strain rate increases. It is simply a measure of the resistance of the fluid to flow.

The more complex way to represent the first equation is:

$$\tau_{yx} = -\mu \frac{dv_x}{dy}$$

where τ_{yx} is shear stress and dv_x/dy is the velocity gradient in the fluid. The equation says that momentum shifts from a high velocity profile to a lower velocity profile. This is the fundamental equation of momentum transfer, which corresponds with the fundamental equations of heat and mass transfer. (Heat flows from a high temperature area to a low temperature area; mass flow from a high concentration to a low concentration.)

One can measure the properties of a material as it responds to different types of flow. Two different types of flow are shear flow and elongational flow. In shear flow the forces act parallel to the plane of the fluid. It assumes that flow occurs as a series of plates that slide past one another. Elongational flow is flow where an element is stretched from an original length to a final length over a period of time, and the forces act perpendicular to the plane. Every material reacts differently to each different type of flow. It is important to know the shear properties for materials that will be experiencing normal flow like flow in pipes. Elongational properties are useful for specialty polymeric processing such as injection molding, melt blowing, and spinning. The properties for both types of flow are important for polymers like PHAs.

PHAs are a class of polymers with diverse properties. They are semi-crystalline thermoplastics, and are synthesized and accumulated in bacteria under unfavorable growth conditions in bioreactors. Individual polymers range from hard and stiff to very elastic. Polymers are chains of monomer units. The basic monomer for PHAs is shown in figure 1.

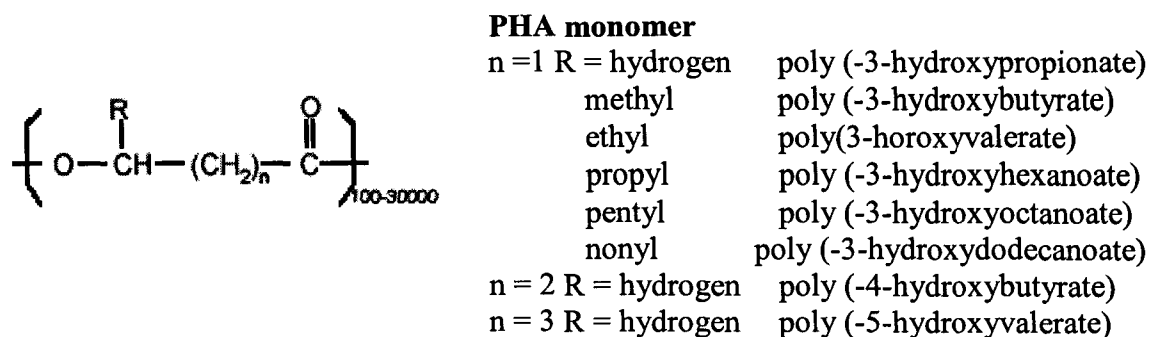


Figure 1. Typical PHA Monomers

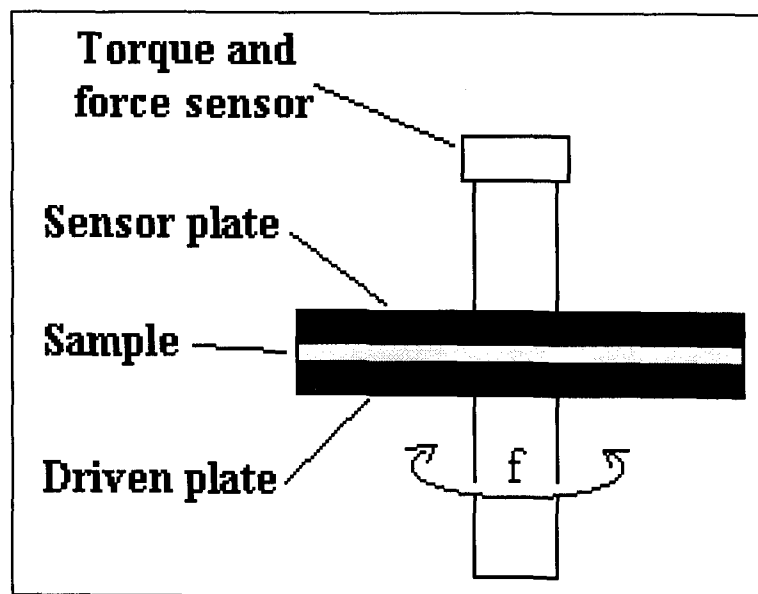


Figure 2. Diagram of Rheometer

Viscosity can be measured in various ways. In this study, a dynamic rheometer (figure 2) is used to measure the complex viscosity. The polymer sample is inserted between two parallel plates. The bottom plate is connected to a shaft, which oscillates the plate at varying angular velocities. The top plate is connected to torque and force transducers, which collect data that ultimately give a viscosity curve.

Shear strain

$$\gamma = \gamma_0 \sin \omega t$$

Shear stress

$$\tau = \tau_0 \sin(\omega t + \delta)$$

Stress wave can be decomposed in two waves

$$\tau = \tau' + \tau'' = \tau_0' \sin \omega t + \tau_0'' \cos \omega t$$

The decomposition suggests two dynamic moduli

G' , elastic (storage) modulus

$$G' = \frac{\tau_0'}{\gamma_0}$$

G'' , viscous (loss) modulus

$$G'' = \frac{\tau_0''}{\gamma_0}$$

Complex modulus

$$G^* = G' + iG''$$

Strain rate

$$\dot{\gamma} = \frac{d\gamma}{dt} = \dot{\gamma}_0 \cos \omega t$$

Dynamic viscosity

$$\eta' = \frac{\tau_0''}{\dot{\gamma}_0} = \frac{G''}{\omega}$$

where ω is angular velocity

$$\omega = 2\pi f$$

where f is the frequency of oscillations.

Complex viscosity

$$\eta^* = \sqrt{(\eta')^2 + (\eta'')^2} = \sqrt{\left(\frac{G''}{\omega}\right)^2 + \left(\frac{G'}{\omega}\right)^2} = \frac{|G^*|}{\omega}$$

Complex viscosity vs angular velocity (deformation rate) is graphed to give the viscosity curve for a given temperature.

Experimental Method

Three samples of PHA polymers were obtained to be studied. Samples A, B, and C were pellets of varying sizes, colors, and consistency. Sample A was a small, cream-colored pellet that was creamy when melted. It was measured at 170, 180, 190, and 200°C.

Sample B was a medium-sized, beige-colored pellet. It was measured at 180, 190, and 200°C.

Sample C was a larger, brown-colored pellet. It had a honey-like consistency when melted. It was measured at 180, 185, and 190°C.

Temperatures were chosen by knowledge of the melting point by a differential scanning calorimetry measurement. The melting point for polymer C was measured to be 163°C. The assumption was made that the other sample had similar melting points. Information on the website of the company that produces PHAs indicated that the polymers were thermally unstable above 200°C. Tests confirmed that the three polymer samples may have been starting to degrade at around 200°C—the viscosities were very low at that point.

All tests were run at a strain rate of 1%. A dynamic strain sweep test was run on PHA A to confirm that the viscosities changed very little with varying strain rates. It was assumed that the other polymers would have similar results and that changing the strain rate would change the viscosity little.

Results and Discussion

Figure 3 shows the results from the dynamic strain sweep for PHA A. They show that the strain rate does not affect the viscosity very much.

The complex viscosity for PHA A is shown in Figure 4. For a given temperature, the viscosity does not show a great amount of change. Therefore, the sample shows Newtonian behavior, but has slight shear thinning (a decrease in viscosity as deformation rate increases). Viscosity changes a great deal between temperatures for a mere 10°C temperature change. Other polymers would need a 25°C temperature change to get the same change in viscosity.

Dynamic moduli for PHA A are shown in Figure 5 for three temperatures: 170, 180, and 190°C. The dynamic moduli, G' and G'' , are also referred to as the elastic and viscous moduli, respectively. Because the viscous modulus, G'' , is higher than the elastic modulus, G' , in all cases, the polymer behaves as a viscous fluid. If the elastic modulus is higher instead, the polymer would behave as an elastic material like a bouncy ball in that region. An elastic material retains its original form when deformed.

A master curve can be derived from the complex viscosity data for any polymer. Using an Arrhenius dependence, one can shift all the viscosities to the same curve by finding the activation energy for flow. Once the dependence is found, the viscosity can be estimated at any temperature within the range of temperatures tested. The master curve for polymer A is shown in Figure 6.

The results for PHA B are similar to PHA A and are shown in Figures 7 and 8. The viscosity is lower for PHA B than PHA A. The results for PHA C are not shown because they were very similar to PHA A and B, just slightly lower.

Figure 9 is a comparison of PHA samples to other types of polymers. The other polymers are extrusion-grade polypropylene, melt blowing polypropylene (35, 700, and 1500 melt flow rates), high density polyethylene, low-density polyethylene, and a lyocell solution.

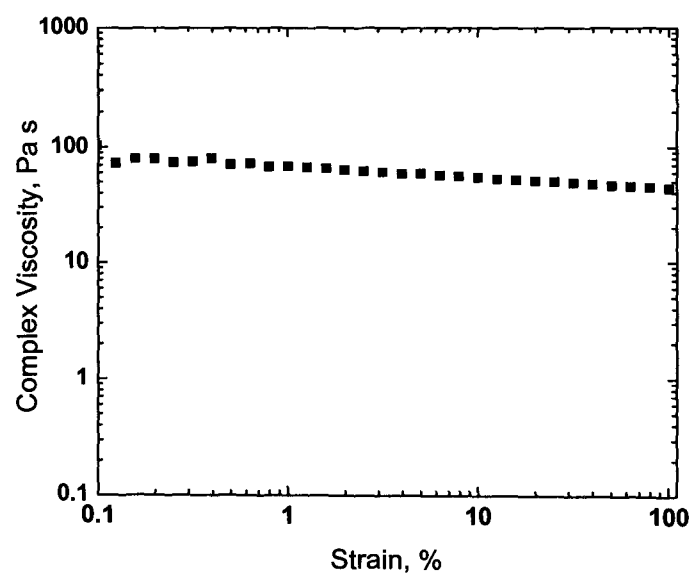


Figure 3. Dynamic Strain Sweep for PHA A

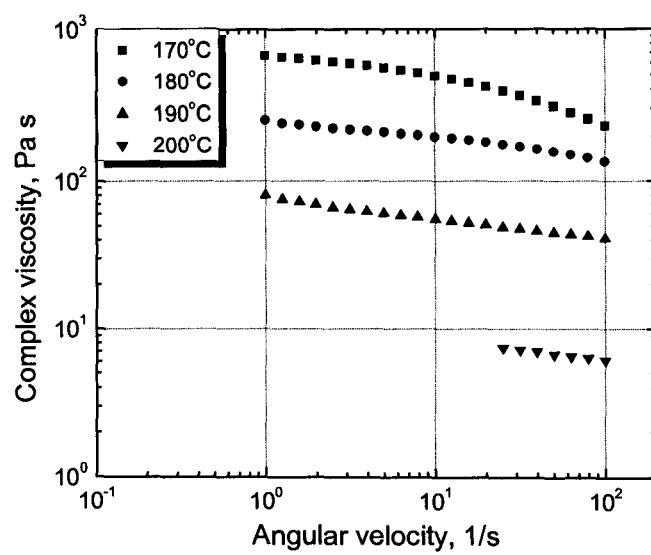
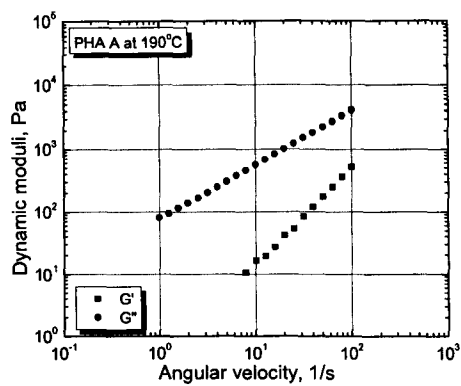
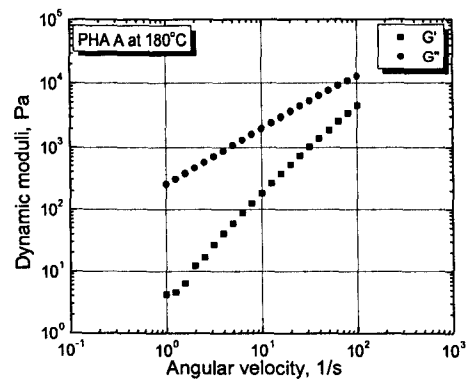


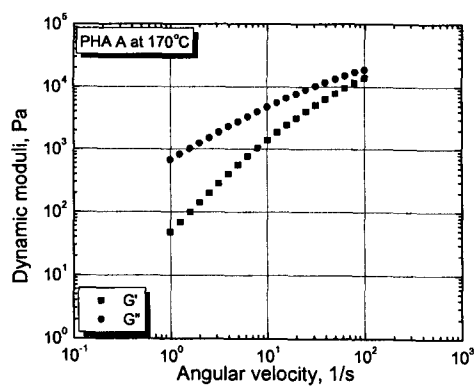
Figure 4. Complex Viscosity of PHA A



(a) 190



(b) 180



(c) 170

Figure 5. Dynamic Moduli of PHA A

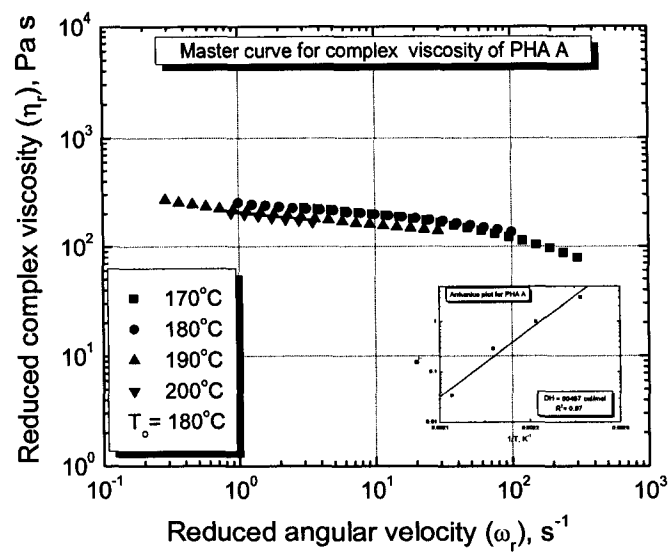


Figure 6. Master Curve for PHA A

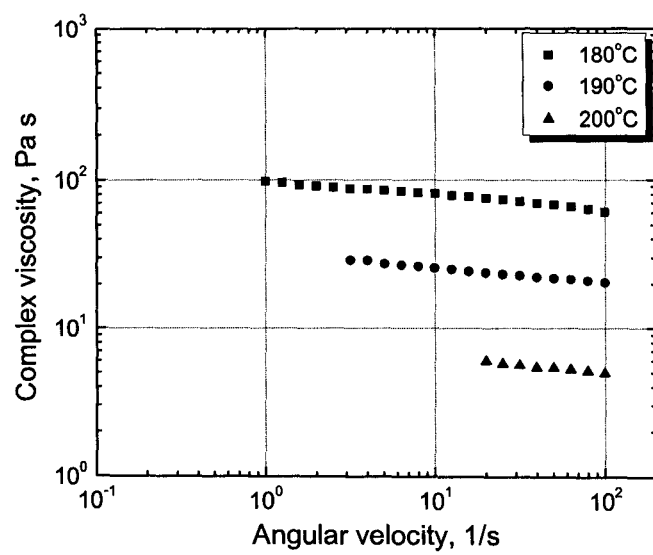
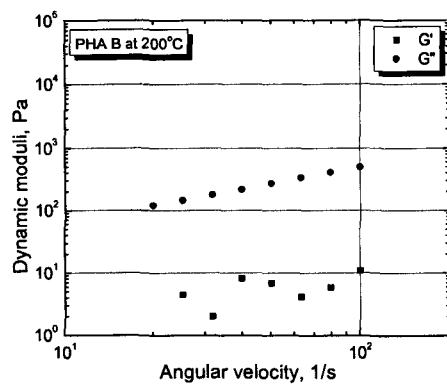
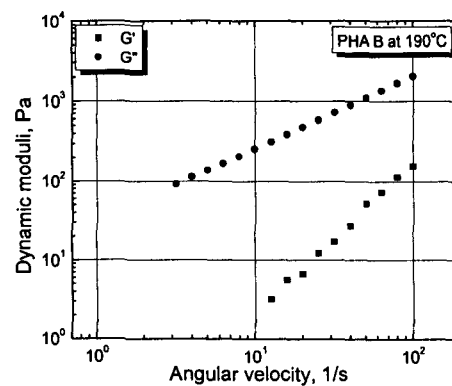


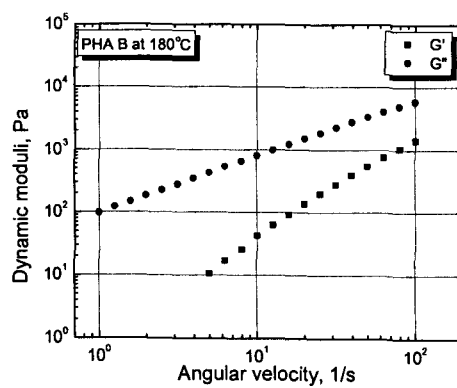
Figure 7. Complex Viscosity of PHA B



(a) 200



(b) 190



(c) 180

Figure 8. Dynamic Moduli of PHA B

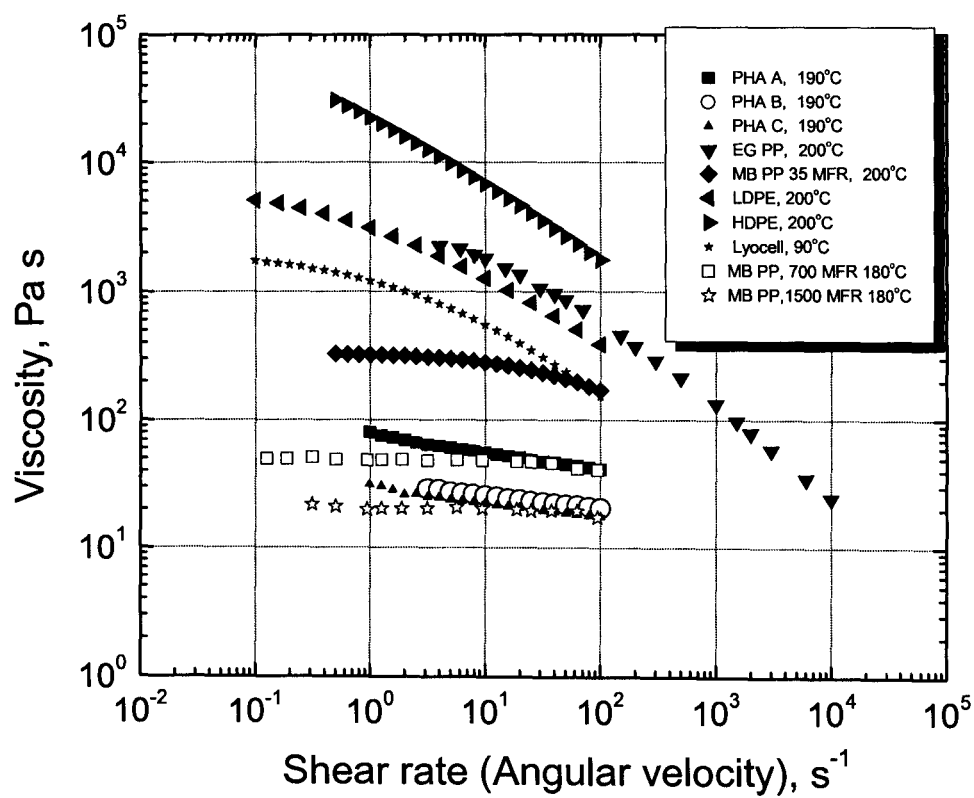


Figure 9. Comparison of Different Polymers

Conclusions

Several conclusions can be drawn from the results of this study. The conclusions also lend themselves to advising future work to be done on PHA resins.

The resins all show Newtonian behavior, which is characterized by constant viscosity. While all of the samples did have decreasing viscosity with increasing angular velocity, they did not decrease significantly.

The viscosities of all three resins are lower than the viscosities of melt blowing grade polypropylene (MB PP, 35 MFR), extrusion grade polypropylene (MW 300,000), low density polyethylene, (MW 86,650), and lyocell solution (from a dissolving pulp of DP 670). They are comparable to melt blowing grade polypropylene of 700 and 1500 MFR.

Because the resins have similar viscosities to some melt blowing grade polypropylenes, they are likely useful for processing as non-wovens. Non-wovens are used in numerous commercial products. Examples are diapers, feminine products, and medical gowns. The benefits of replacing currently-used non-woven products with those made from biodegradable polymer are endless.

Future work on PHAs includes furthering the work done with the ACER capillary rheometer to determine the behavior of PHAs at even higher deformation rates, rates that would be applicable in non-woven processing. Other possible work is pilot testing of the analyzed resins using the processing capabilities of the TANDEC center on The University of Tennessee's campus. TANDEC stands for Textiles And Nonwovens Development Center. More information can be found about TANDEC at web.utk.edu/~tandec.

References

1. Metabolix Inc., www.metabolix.com.
2. J.R. Collier, O. Romanoschi, and Simioan Petrovan, Elongational Rheology of Polymer Melts and Solutions. *Journal of Applied Polymer Science*, 69, 2357-2367(1998).
3. Bird, R. B., Stewart, W. E., and Lightfoot, E. N., *Transport Phenomena*, Second Edition, John Wiley, 2002.
4. Bird, R. B., Armstrong, R. C., and Hassager, O., *Dynamics of Polymeric Liquids*, Vol. 1. Fluid Mechanics, John Wiley, 1987.
5. "Production of Polyhydroxyalkanoates, a biodegradable polymer," Ojumu et al. *African Journal of Biotechnology*. Jan. 2004.